



# FeVO<sub>4</sub> as a highly active heterogeneous Fenton-like catalyst towards the degradation of Orange II

Jingheng Deng, Jingyuan Jiang, Yuanyuan Zhang, Xiaoping Lin, Changming Du, Ya Xiong\*

School of Environmental Science and Engineering, Sun Yat-Sen University, Guangzhou 510275, PR China

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## ABSTRACT

The iron vanadate, FeVO<sub>4</sub>, was prepared and characterized by X-ray diffraction (XRD), Brunauer–Emmett–Teller (BET) surface area, X-ray photoelectron spectroscopy (XPS), scanning electron microscopy (SEM). It was found that FeVO<sub>4</sub> could effectively catalyze H<sub>2</sub>O<sub>2</sub> to generate active hydroxyl radical •OH, which was confirmed with electron spin resonance (ESR) spin-trapping technique. Therefore, it was employed as a heterogeneous Fenton-like catalyst in the present contribution, and its catalytic activity was mainly evaluated in terms of the degradation efficiency of Orange II. Compared with the conventional heterogeneous Fenton-like catalysts, α-Fe<sub>2</sub>O<sub>3</sub>, Fe<sub>3</sub>O<sub>4</sub> and γ-FeOOH, FeVO<sub>4</sub> possessed a much higher catalytic activity. The high catalytic activity possibly involved in a special two-way Fenton-like mechanism, that is, the activation of H<sub>2</sub>O<sub>2</sub> by both Fe(III) and V(V) in FeVO<sub>4</sub>. Moreover, FeVO<sub>4</sub> possessed a wide applicable pH range and its catalytic activity was slightly affected by the solution pH values in the range of 3–8.

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## 1. Introduction

Fenton technology is widely studied and reported as an interesting alternative for the treatment of industrial wastewater containing non-biodegradable organic pollutants. However, the homogeneous Fenton process has significant disadvantages: (i) iron ions have to be separated from the system at the end of the process by precipitation, which is expensive in labor, reagents and time; (ii) it is limited by a narrow pH range (pH 2–3); and (iii) iron ions may be deactivated due to the complexation with some iron complexing reagents, such as phosphate anions [1] and some intermediate oxidation products, etc. [2]. To overcome these disadvantages of homogeneous Fenton process, heterogeneous Fenton and Fenton-like catalysts have recently received much attention. To date, the investigations was mainly focused on three types of materials: (i) iron–oxygen series of compounds, such as α-Fe<sub>2</sub>O<sub>3</sub>, α- and γ-FeOOH [3,4], Fe<sub>3</sub>O<sub>4</sub> [5] and Fe<sup>0</sup>/Fe<sub>3</sub>O<sub>4</sub> [6], etc.; (ii) Fe-immobilized materials in which Nafion membrane [7,8], polyethylene film [9], fly ash [10], polyelectrolyte microshells [11], carbon [12], resin [13,14], silica [15–17], clay [18–20] and Al<sub>2</sub>O<sub>3</sub> [21] were used as the solid matrix for immobilizing Fe; and

(iii) natural Fe-containing materials, such as limonite and goethite, etc. [22].

These heterogeneous Fenton and Fenton-like catalysts were demonstrated to be useful to treat various organic pollutants in water over a wider applicable pH range. However, many of them did not show favorable catalytic activity [2]. For example, when using goethite as heterogeneous Fenton catalyst in the degradation of 1,2-benzenediol, 2-aminophenol and 2,3-dihydroxybenzoic acid, only about 10% TOC removal were achieved after 2 h [23]. Hence, UV and/or visible light are often used to accelerate the degradation of the pollutants catalyzed by these heterogeneous Fenton catalysts. The application of these lights needs specific equipment and additional cost. In this sense, it is a challenging issue to develop novel heterogeneous Fenton or Fenton-like catalysts with higher catalytic activity.

It was noticed that the design of the present heterogeneous Fenton-like catalysts was mainly concentrated on modifying the physical and chemical environment of the iron. No attention was paid to which if the anions combined with iron cation in heterogeneous Fenton catalysts possessed the Fenton-like catalytic activity. This situation inspired us to search for a Fe-containing compound in which both iron ions and anions could simultaneously activate H<sub>2</sub>O<sub>2</sub> towards the oxidation of pollutants. This kind of compounds was referred to as two-way Fenton-like catalyst in this paper.

\* Corresponding author. Tel.: +86 20 84115556; fax: +86 20 39332690.  
E-mail address: [cesxya@mail.sysu.edu.cn](mailto:cesxya@mail.sysu.edu.cn) (Y. Xiong).

It was reported that vanadium (V) in many compounds, such as  $V_2O_5$  [24],  $H_2VO_4$  [25],  $\gamma$ -1,2- $H_2SiV_2W_{10}O_{40}$  [26], V-ALPO [27], V-MCM [28],  $V_xSi_{4x}O_{6.4x}$  [29] and VO cores-containing complexes [30], could heterogeneously or homogeneously catalyze the oxidation of various organic and inorganic compounds in the presence of  $H_2O_2$  through Fenton-like pathways [31]. These compounds included halides, sulfur dioxide, thioethers, alkenes, alcohols and aromatic or aliphatic hydrocarbons [32]. Moreover, vanadate(V) could be combined with iron ion to form the rather stable solid substances in acidic condition. Therefore, there is a possibility that the compound containing iron ion and vanadate anion may be employed as the two-way Fenton-like heterogeneous catalyst.

A simple Fe–V compound,  $FeVO_4$ , was selected as the first example of the potential two-way Fenton-like catalysts in our project. The study was mainly focused on three aspects: (i) the catalytic performance of  $FeVO_4$ ; (ii) the stability of  $FeVO_4$ ; (iii) the catalytic mechanism of  $FeVO_4$ . In addition, Orange II was selected as a model contaminant because it is non-biodegradable and used extensively in textile industry.

## 2. Experimental

### 2.1. Materials

Analytical grade of ammonium metavanadate, iron(III) nitrate nona-hydrate and hydrogen peroxide solution (30%, w/v) were purchased from Guangzhou Chemical Reagent Company, China. Ferric oxide and ferrous oxide were obtained from Tianjin Kermel Chemical Reagent Co. Ltd., China.  $\gamma$ - $FeOOH$  has been synthesized followed the procedure by Hall et al. [33]. 5,5-Dimethyl-1-pyrroline-*N*-oxide (DMPO) was purchased from Sigma. The Orange II was a commercial dye (Hengrun Dyestuff Chemical Co., Ltd., Guangzhou) and used without further purification.

### 2.2. Preparation of catalyst

$FeVO_4$  was prepared by a reported wet chemical process [34]. A 0.26 M solution of iron nitrate was quickly poured into a  $4.27 \times 10^{-2}$  M solution of ammonium metavanadate under stirring and maintained at 75 °C for 1 h. The resulting precipitate was separated by pumping filtration, and sequentially washed with ultrapure water and acetone. Finally, naturally dried  $FeVO_4$  was calcined in a muffle furnace at 100 °C, 200 °C, 300 °C, 400 °C and 500 °C for 2 h, respectively.

### 2.3. Characterization of iron vanadate

The XRD patterns of the catalyst were obtained by using D/max 2200 vpc Diffractometer (Rigaku Corporation, Japan) with a  $Cu K_\alpha$  radiation at 40 kV and 30 mA. Specific BET surface area and BJH method for pore size distribution were determined with a Micromeritics ASAP 2010 apparatus by nitrogen adsorption at 77 K. The SEM was performed on gold-coated samples using a JSM-6330F-mode Field Emission Scanning Electron Microscope (JEOL, Japan). ESR signals of radicals trapped by DMPO were obtained on a Bruker model ESP 500E electron paramagnetic resonance spectrometer. XPS analysis was performed with a VG ESCALAB 250 spectrometer with an Al  $K_\alpha$  monochromatized radiation operated at 150 W (15 kV, 10 mA). Binding energies were calibrated versus the carbon signal at 284.6.0 eV. The electrokinetic mobility of the  $FeVO_4$  samples in aqueous solutions was measured by using an electrophoretic light scattering spectrophotometer (JS94H, Shanghai zhongchen, China).

### 2.4. Experimental procedures

All the experiments were carried out in a cylindrical Pyrex vessel (60 mL). In a typical run, the reaction suspension was prepared by adding a given amount of  $FeVO_4$  powder into 40 mL Orange II solution which has been adjusted to the desired pH value by NaOH or  $H_2SO_4$ . Prior to reaction, suspension was sonicated for 5 min and magnetically stirred in the dark for 30 min to establish the adsorption/desorption equilibrium. Fenton-like reaction was initiated by adding a known concentration of  $H_2O_2$  to the solution with constant aeration acting as agitation. Samplings were taken at a given time intervals during the reaction. Then samples were analyzed immediately after filtration through 0.22  $\mu$ m Millipore membrane filters to remove suspended particles. The pH of Orange II solution was measured by using a PHS-3C pH meter (Rex Instrument Factory, Shanghai, China). The test of  $FeVO_4$  stability was conducted in a film reactor [35].

### 2.5. Analytical methods

The concentration of Orange II was analyzed on UV–vis spectrophotometer (UV-3150, Shimadzu) with its adsorption at 484 nm. The atomic ratio of  $FeVO_4$  and the leaching concentrations of Fe and V in the solution were measured by inductively coupled plasma optical emission spectrometry (ICP-OES, optima 5300DV, Perkin-Elmer).

The concentration of  $\cdot OH$  was determined by using a recently reported method [36]. An aqueous solution of benzene was mixed with  $FeVO_4$  thoroughly and transferred into the cylindrical reactor. The concentration of benzene was 10 mM and the catalyst was suspended at 0.5 g  $L^{-1}$  in the solution. Different amounts of  $H_2O_2$  were added into the aqueous solution. After the run, the samples were separated from  $FeVO_4$  and the phenol concentrations were analyzed.

## 3. Results and discussion

### 3.1. Characterization of $FeVO_4$

As  $Fe(NO_3)_3$  was mixed with  $NH_4VO_3$  according to a molar ratio of 1:1, a yellow solid was rapidly formed and the pH value of the resulting solution at the end of the reaction was 2.1. The Fe/V molar ratio of the dried yellow solid at 100 °C was determined to be 0.999 by ICP-OES and its average particle size from its SEM micrographs (figure not shown) was estimated as about 100 nm.

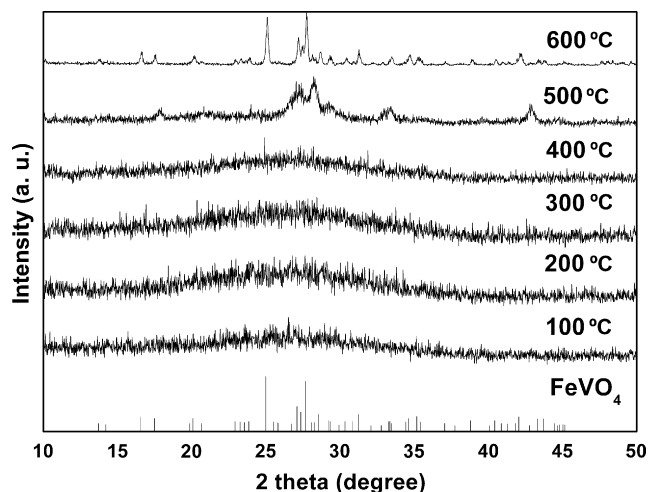


Fig. 1. XRD spectra of  $FeVO_4$  thermally treated at different temperatures.

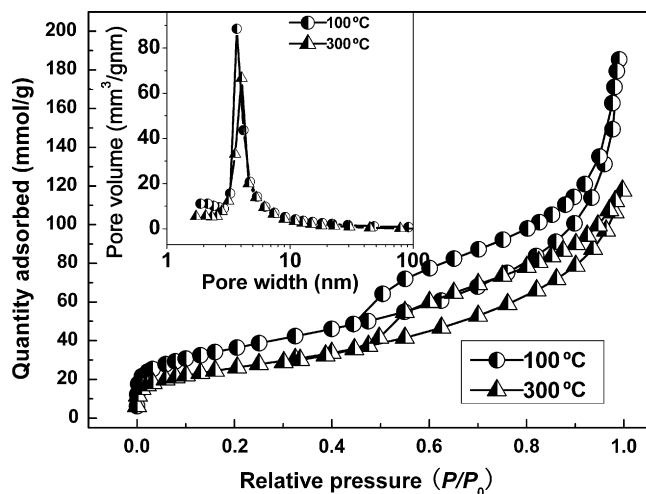


Fig. 2.  $N_2$  adsorption/desorption isotherms of  $FeVO_4$  at 77 K. Inset: pore size distribution of  $FeVO_4$ .

The ratio was much closer to the theoretical stoichiometry of  $FeVO_4$ . The XRD pattern of the compound calcined at 100 °C presented a weak and broad peak at  $2\theta$  angles of about 25° (Fig. 1), suggesting that the yellow solid is a kind of amorphous compound. However, with the increasing calcination temperature its XRD pattern became clearer. At 500 °C and 600 °C, three intense diffraction peaks were distinctly observed at  $2\theta$  angle of 25.04°, 27.66° and 27.16°, respectively. The diffraction peaks were well matched with the published JCPDS data (JCPDS file no: 38–1372) for triclinic  $FeVO_4$ .

Fig. 2 gives the nitrogen adsorption isotherms and the pore size distribution of  $FeVO_4$  calcined at 100 °C and 300 °C. The isotherms show a typical type IV pattern with an inflection of nitrogen adsorbed volume at  $P/P_0$  about 0.47 (type H 3 hysteresis loop), indicating the existence of mesopores. The BET surface area and pore volume of  $FeVO_4$  are 128.3 m<sup>2</sup> g<sup>−1</sup> and 0.287 cm<sup>3</sup> g<sup>−1</sup> for 100 °C, 93.8 m<sup>2</sup> g<sup>−1</sup> and 0.182 cm<sup>3</sup> g<sup>−1</sup> for 300 °C, respectively. The data suggests that the BET surface area and pore volume of  $FeVO_4$  decrease gradually with the increase of thermal treatment temperature. At the same time, the pore size distribution turns narrow gradually with the increase of thermal treatment temperature (Fig. 2 inset).

Generally, the catalytic activity of solid catalyst greatly depends on its surface charge besides surface area [37]. To examine the surface charge properties of  $FeVO_4$ , its Zeta potentials were determined at various pH values. The  $pH_{iep}$  (isoelectric point) of  $FeVO_4$  was located at 4.15. The  $pH_{iep}$  is lower than that of  $\alpha$ - $Fe_2O_3$  (5.2–8.6),  $FeOOH$  ( $6.7 \pm 0.2$ ) and  $Fe_3O_4$  ( $6.5 \pm 0.2$ ) [38]. Thus, the surface of  $FeVO_4$  was negatively charged over pH 4.15, which would benefit the transformation of  $H_2O_2$  to hydroxyl radicals in heterogeneous catalysis due to the electrophilic characteristics of aqueous  $H_2O_2$  [4]. With respect to the  $pH_{iep}$  value,  $FeVO_4$  was considered as the better candidate for a solid catalyst comparing with iron oxides.

### 3.2. Catalytic activity of $FeVO_4$

The degradation process of Orange II catalyzed by  $FeVO_4$  with  $H_2O_2$  was monitored by UV–vis spectra. As shown in Fig. 3, the original absorption of Orange II mainly consists of three well-resolved absorption peaks at 484 nm, 310 nm and 228 nm and two shoulders at 254 nm and 430 nm. The peaks at 310 nm and 228 nm, and the shoulder at 254 nm are assigned to the aromatic rings. The peak at 484 nm and the shoulder at 430 nm are assigned to the conjugated structure formed by the azo bond [39]. As the

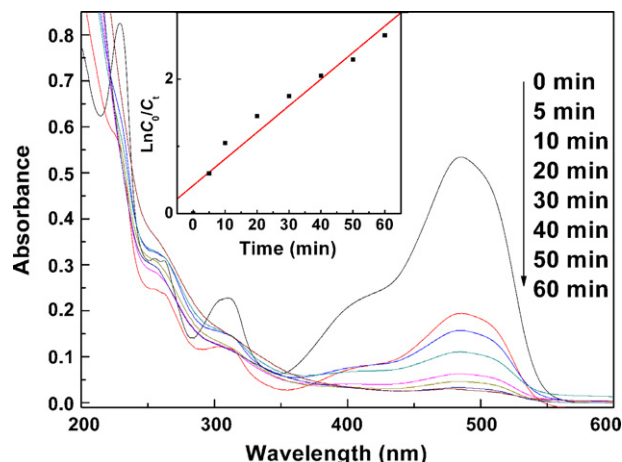


Fig. 3. The UV–vis spectral changes of Orange II ( $FeVO_4$ : 0.5 g L<sup>−1</sup>;  $H_2O_2$ : 15 mM; Orange II: 100 mg L<sup>−1</sup> and initial pH 6.1; inset: the first-order linear relationship).

reaction proceeds, the three characteristic absorption peaks decreased dramatically and nearly disappeared after 60 min, showing that the chromophore and conjugated  $\pi^*$  system were completely destroyed. If the change of absorption peak at 484 nm was applied to evaluate the degradation of Orange II, the first-order linear relationship was obtained, as showed by the plots of  $\ln(C_0/C_t)$  versus reaction time (the inset of Fig. 3). The rate constant was calculated to be 0.0395 min<sup>−1</sup> and the optimal  $H_2O_2$  dose was 15 mM.

It is difficult to compare the catalytic activity of various heterogeneous Fenton catalysts from literature data due to the difference of experimental conditions. In the present study,  $FeVO_4$  and other three heterogeneous Fenton-like catalysts mentioned frequently in references,  $\alpha$ - $Fe_2O_3$ ,  $Fe_3O_4$  and  $\gamma$ - $FeOOH$ , were employed to catalyze the degradation of Orange II with  $H_2O_2$  at identical conditions to more clearly understand the catalytic activity of  $FeVO_4$ . The experimental results (data not shown) indicated that  $\alpha$ - $Fe_2O_3$  and  $Fe_3O_4$  could hardly catalyze  $H_2O_2$  to degrade Orange II, which was consistent with the result observed by Lim et al. [40]. For  $\gamma$ - $FeOOH$ , only a degradation efficiency of 35.8% were observed after 60 min. In contrast, the degradation efficiency of  $FeVO_4$  reached 92.9%, which was 1.6 times more than that of the former catalysts. This comparison was based on the identical weight of catalysts. If the comparison was based on the amount of iron, the catalytic efficiency of  $FeVO_4$  would reach as high as 5.6 times relative to that of other three Fenton-like catalysts. It should be noted that it is different to compare the Fenton-like activity of different heterogeneous catalysts due to leaching difference for these catalysts. We tested the catalytic activation of filtration for the  $FeVO_4$ - $H_2O_2$ -Orange II slurry, and just little of Orange II degradation was found. Therefore, it was believed that the  $FeVO_4$ - $H_2O_2$  system mainly originated from solid  $FeVO_4$ , not from the leached ions.

However, it was observed that the catalytic activity of  $FeVO_4$  was considerably dependent on the calcination temperature (Fig. 4). It decreased with the increasing of calcination temperature, especially above 300 °C. For example, the degradation efficiency could reach 94.2% after 60 min for the untreated thermally  $FeVO_4$ , while 79.2% for the catalyst claimed at 350 °C for 2 h. This result was rather consistent with the change of specific surface area under different calcination temperature, as shown in Fig. 4. Therefore, the decrease in catalytic activity of  $FeVO_4$  could be simply attributed to the decrease specific surface area of the catalyst. And the drying process of  $FeVO_4$  should be controlled at

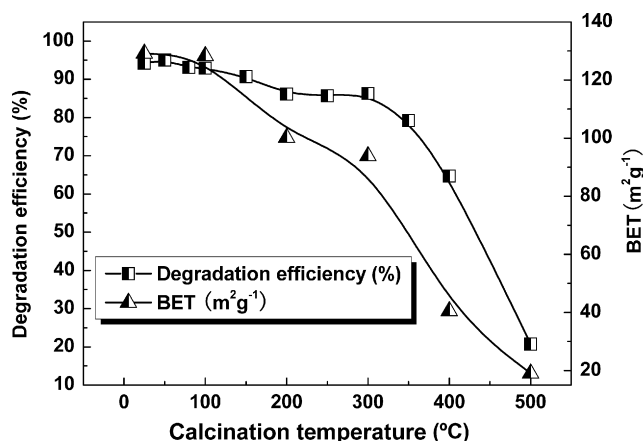


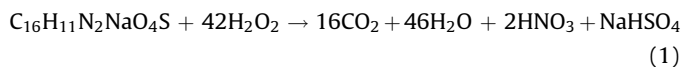
Fig. 4. Degradation efficiency of Orange II after 60 min ( $\text{FeVO}_4$ :  $0.5 \text{ g L}^{-1}$ ;  $\text{H}_2\text{O}_2$ :  $15 \text{ mM}$ ; Orange II:  $100 \text{ mg L}^{-1}$  and initial pH 6.1) and  $S_{\text{BET}}$  of  $\text{FeVO}_4$  thermally treated for 2 h at different temperatures.

temperature as low as possible in order to keep a higher catalytic activity.

### 3.3. Applicable pH range

As mentioned above, another motive to develop new heterogeneous Fenton-like catalyst is to extend the pH range of  $\text{Fe(III)}$  application, in addition to enhancing catalytic activity. Catalytic activity of  $\text{FeVO}_4$  was slightly affected by the solution pH values in the range of 3–8. Only when the solution pH was over 10.4, the catalytic activity of  $\text{FeVO}_4$  was apparently decreased (data not shown). Thus, no pH adjustment of the medium was needed for effective oxidation over the wider pH range. The pH range of  $\text{FeVO}_4$  with high activity is higher than that of some reported heterogeneous Fenton-like catalyst [41].

It was also observed that the pH value of the reaction solution is continuously decreasing during the reaction process and finally located in a more acidic range. The acidification of the solution was not simply attributed to the generation of  $\text{NaHSO}_4$  and/or  $\text{HNO}_3$  during the degradation process based on the reaction (1) [18]. In fact, though pollutants do not contain S and N elements, and no inorganic acids form in the degradation process, many organic acids will be also generated, leading to the decrease of the pH value for the system [4]. The result was further confirmed by an additional experiment using phenol as testing pollutant. In addition, considering that  $\text{H}_2\text{O}_2$  can automatically decompose to  $\text{O}_2$  at high pH value and the discharged effluent is generally regulated in pH 6–9,  $\text{FeVO}_4$  is suggested to be preferably applied at ca. pH 6–8, thus no or less adjustment of pH value is needed before discharge.



### 3.4. Stability of $\text{FeVO}_4$

The above discussions are only on the basis of a single experiment for  $\text{FeVO}_4$ . From the view of actual application, the long-term stability of  $\text{FeVO}_4$  is very important. Therefore, the leaching characteristics and the activity variation of  $\text{FeVO}_4$  in cycles were especially concerned. For the convenience of repeatable use,  $\text{FeVO}_4$  was immobilized on glass plate. The Fenton-like catalytic efficiency of  $\text{FeVO}_4$  towards the degradation of Orange II did not obviously change in first six runs.

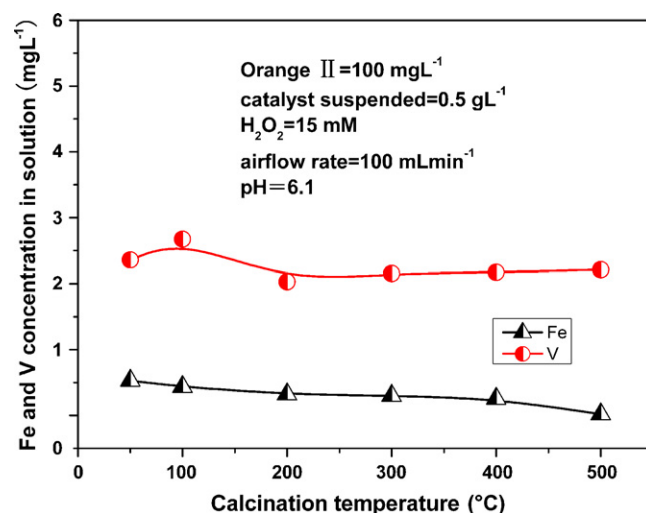


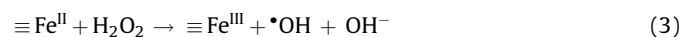
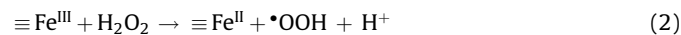
Fig. 5. Concentrations of leached Fe and V for  $\text{FeVO}_4$  thermally treated at different temperature in the reaction processes.

It can be seen from Fig. 5 that the concentration of the leached  $\text{Fe(III)}$  for  $\text{FeVO}_4$  dried at  $50^\circ\text{C}$  is higher than that at  $100^\circ\text{C}$ . For example, the leaching amounts of  $\text{Fe(III)}$  are  $0.528 \text{ mg L}^{-1}$  at  $50^\circ\text{C}$  and  $0.434 \text{ mg L}^{-1}$  at  $100^\circ\text{C}$ , respectively. It should be noted that the leaching of Fe-ions, although it takes place, remained below  $1 \text{ mg L}^{-1}$  which is acceptable according to EU discharge standards ( $<2 \text{ ppm}$ ) [42]. However, the leaching of V-ions was undesirable as shown in Fig. 5. The concentration of leached vanadium for  $\text{FeVO}_4$  was determined to be about  $2.5 \text{ mg L}^{-1}$ . It is noteworthy that the oxidation of organic pollutants can generally generate organic and/or inorganic acids, probably leading to the acidification of the treated solution, as discussed above. Thus, Fenton-like catalysts experience more acidic conditions sometimes, although their initial pH values are neutral or basic. The leaching could attribute to the coordination effect of organic acid generated during the degradation of Orange II, as observed for other solid Fenton-like catalysts [43].

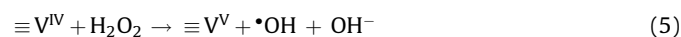
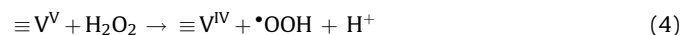
This leaching will be disadvantageous to in the long-term application of  $\text{FeVO}_4$ , although these  $\text{Fe(III)}$  leaching amounts were not enough to significantly affect their catalytic activity in six repetitive runs. It is necessary to solve the decrease the desirable leaching of vanadium before  $\text{FeVO}_4$  is actually employed.

### 3.5. Approaching to the catalytic mechanism

The mechanism of Fenton-like reaction is still far from fully understanding, nevertheless, the most popular candidates to activate  $\text{H}_2\text{O}_2$  are involved in the following two reactions [44]:

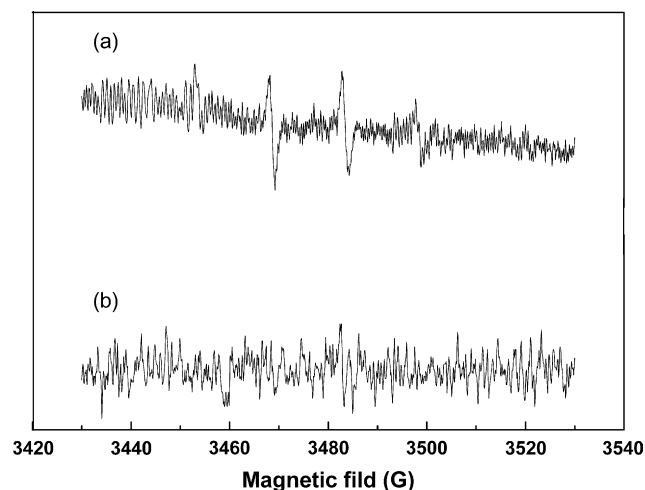


Similar to the Fenton-like reaction, the activation of  $\text{V(V)}$  compound towards  $\text{H}_2\text{O}_2$  is believed to follow the two steps below [31,45]:



Both mechanisms are related to an active free radical  $\cdot\text{OH}$ . To investigate whether the  $\text{FeVO}_4\text{--H}_2\text{O}_2$  system could produce radical  $\cdot\text{OH}$  like other catalysts containing  $\text{Fe(III)}$  or  $\text{V(V)}$  or not, the ESR





**Fig. 6.** DMPO spin-trapping ESR spectra of hydroxyl radicals: (a)  $0.5 \text{ g L}^{-1} \text{FeVO}_4$ ,  $2 \text{ mM H}_2\text{O}_2$ ;  $0.1 \text{ mM Orange II}$ ; (b)  $2 \text{ mM H}_2\text{O}_2$ ;  $0.1 \text{ mM Orange II}$ .

spectroscopy, an effective method for the identification of active radicals, of  $\text{FeVO}_4\text{--H}_2\text{O}_2$  system was determined. The ESR spectrum (Fig. 6) exhibits a 4-fold characteristic peak of  $\text{DMPO}\cdot\text{OH}$  adducts with an intensity ratio of 1:2:2:1. The result clearly indicated that  $\text{FeVO}_4$  could mediate  $\text{H}_2\text{O}_2$  to generate  $\cdot\text{OH}$  [46]. However, it is unknown whether the  $\cdot\text{OH}$  was produced with  $\text{Fe(III)}$ ,  $\text{V(V)}$  or simultaneously with them in  $\text{FeVO}_4$ . The quantitative determination results of  $\cdot\text{OH}$  concentrations seemed beneficial to understand the origin of  $\cdot\text{OH}$ . The other two kinds of  $\text{Fe--V--O}$  compounds,  $\text{Fe}_2\text{V}_4\text{O}_{13}$  [47] and  $\text{FeV}_3\text{O}_9$  [48], were prepared by the method in the previous report.  $\text{Fe--V--O}$  compounds and  $\text{FeVO}_4$  were applied to activate  $\text{H}_2\text{O}_2$  for quantitatively producing  $\cdot\text{OH}$ . By comparison, it was found that, with respect to the identical amount of  $\text{V(V)}$ , the  $\cdot\text{OH}$  concentrations increased with the increase of the  $\text{Fe(III)}$  amount in the three catalysts. When all the catalysts containing  $0.0715 \text{ mmol V(V)}$  were applied, the concentrations of  $\cdot\text{OH}$  for  $\text{FeV}_3\text{O}_9$ ,  $\text{Fe}_2\text{V}_4\text{O}_{13}$  and  $\text{FeVO}_4$  were determined to be  $0.32 \text{ mg L}^{-1}$ ,  $0.61 \text{ mg L}^{-1}$  and  $1.26 \text{ mg L}^{-1}$ , respectively. This fact suggested that the  $\text{Fe(III)}$  in  $\text{FeVO}_4$ , like many other compounds containing  $\text{Fe(III)}$ , could activate  $\text{H}_2\text{O}_2$  to generate  $\cdot\text{OH}$ .

Further determination showed, with respect to the identical amount of  $\text{Fe(III)}$ , the  $\cdot\text{OH}$  concentration also increased with the increasing  $\text{V(V)}$  amount of the used catalysts. However, the increase was not as obvious as that with  $\text{Fe(III)}$ . For example, for all the catalysts containing  $0.0715 \text{ mmol Fe}$ , the concentrations of  $\cdot\text{OH}$  for  $\text{FeVO}_4$ ,  $\text{FeV}_2\text{O}_5$  and  $\text{FeV}_3\text{O}_8$  were determined to be  $1.26 \text{ mg L}^{-1}$ ,  $1.45 \text{ mg L}^{-1}$  and  $1.64 \text{ mg L}^{-1}$ , respectively, which meant that an increasing of  $0.0715 \text{ mmol V(V)}$  just lead to the formation of  $0.19 \text{ mg L}^{-1}$  additional  $\cdot\text{OH}$ . The experimental result was an indirect evidence that  $\text{V(V)}$  of  $\text{FeVO}_4$ , like many other containing- $\text{V(V)}$  compounds, could also catalyze  $\text{H}_2\text{O}_2$  to generate  $\cdot\text{OH}$ . The catalytic activity of the  $\text{V(V)}$  in  $\text{FeVO}_4$  seemed lower than that of  $\text{Fe(III)}$ , nevertheless, it is difficult presently to distinguish how many  $\cdot\text{OH}$  radicals produced by  $\text{Fe(III)}$  or  $\text{V(V)}$ .

X-Ray photoelectron spectroscopy (XPS) is a versatile surface analysis technique that can be used for chemical states analysis. To characterize the oxidation state of the  $\text{Fe}$  and  $\text{V}$  in  $\text{FeVO}_4$  before and after Fenton-like degradation Orange II, the XPS testing with high-resolution. The result shows that binding energy (BE) for  $\text{Fe}2\text{p}_{3/2}$  and  $\text{V}2\text{p}_{3/2}$  in unused  $\text{FeVO}_4$  is  $711.19 \text{ eV}$  and  $517.31 \text{ eV}$ , respectively. This corresponds to  $\text{Fe(III)}$  and  $\text{V(V)}$  [49,50]. However, the result shows that BE for  $\text{Fe}2\text{p}_{3/2}$  and  $\text{V}2\text{p}_{3/2}$  in catalyst after 1 h of reaction is  $710.91 \text{ eV}$  and  $517.23 \text{ eV}$ . It is observed the

binding energy of  $\text{Fe}2\text{p}$  and  $\text{V}2\text{p}$  doublet slightly shifted to lower BE value after Fenton-like degradation Orange II, which may be seen as due to the transformation of  $\text{Fe(III)}$  to  $\text{Fe(II)}$  and  $\text{V(V)}$  to  $\text{V(IV)}$  after used  $\text{FeVO}_4$  [15,51].

Additionally, it was found that  $\text{FeVO}_4$  could be completely dissolved in sulfuric acid solution at pH 0.8. With the addition of  $\text{H}_2\text{O}_2$ , the solution gradually changed yellow color, and a wider absorption peak appeared at  $450 \text{ nm}$ . The peak was characterized  $-\text{VO(OOH)}$  type species [52,53]. With an attempt to probing the effect of the  $-\text{VO(OOH)}$  on the catalytic activity of  $\text{FeVO}_4$ , a comparable investigation of the catalytic activity of  $\text{FeVO}_4$  and  $\text{Fe(NO}_3)_3$  as homogeneous Fenton-like catalysts at pH 0.8 was carried out. The degradation efficiency of Orange II for  $\text{FeVO}_4$  was higher 48.4% than that for the  $\text{Fe(NO}_3)_3$  after 60 min. The increase of degradation efficiency further confirmed that the  $\text{V(V)}$  in  $\text{FeVO}_4$  could activate  $\text{H}_2\text{O}_2$  to degrade organic pollutants.

Combining these experimental results above with mechanisms proposed by the literatures for other  $\text{Fe(III)}$ - and  $\text{V(V)}$ -containing compounds [31,44,45], the high catalytic activity of  $\text{FeVO}_4$  could be, at least partly, attributed to the two-way catalytic mechanism involved in the  $\text{Fe(III)/Fe(II)}$  and  $\text{V(V)/V(IV)}$  redox couples, as shown in (2)–(3) and (4)–(5).

#### 4. Conclusion

The  $\text{FeVO}_4$  was first tested and used as a heterogeneous Fenton-like catalyst. It was found that  $\text{FeVO}_4$  possess a highly catalytic activity towards the degradation of Orange II in the presence of  $\text{H}_2\text{O}_2$  in a wide pH range, compared with  $\alpha\text{-Fe}_2\text{O}_3$ ,  $\text{Fe}_3\text{O}_4$  and  $\gamma\text{-FeOOH}$ .  $0.5 \text{ mg L}^{-1} \text{FeVO}_4$  could catalyze  $15 \text{ mmol L}^{-1} \text{H}_2\text{O}_2$  to degrade 92.9% of Orange II with a pH value of 6.1 after 60 min. The highly catalytic activity could be attributed to an interesting two-way mechanism, that is, the activation of  $\text{H}_2\text{O}_2$  by both  $\text{Fe(III)}$  and  $\text{V(V)}$  in  $\text{FeVO}_4$  by Fenton-like pathway.

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